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[Second Edition.]

PATENT SPECIFICATION



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COMPLETE SPECIFICATION.

Improvements in and relating to Impregnated Gel for Adsorbing  
Water Vapor.

We, THE SILICA GEL CORPORATION, a corporation organised and existing under the laws of the State of Maryland, located and doing business at 1100, Garrett 5 Building, 239, Redwood Street, Baltimore, Maryland, United States of America, Assignees of ERNEST BALDWIN MILLER and GERALD CHARLES CONNOLLY, citizens of the United States of America, both of above address, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

15 The present invention relates to the adsorption of water vapor and to materials employed for this purpose and the preparation thereof.

20 It is well known that gels such as silica gel are very efficient adsorbents of water vapor even at low vapor pressures.

25 It is the principal object of the present invention to improve the efficiency and activity of such materials for adsorbing water vapor.

According to the present invention an adsorbent for water vapor comprises a solid porous gel whose pores are of a size such that the gel will adsorb water vapor to such an extent as to contain not less than 10% of its own weight of water when in equilibrium with water vapor at 30° C. and a partial pressure of 22 mm. of mercury, impregnated with a dehydrating agent, the adsorption capacity stated being that of the gel before impregnation.

According to a feature of the invention, the solid porous gel is silica gel.

40 Although it is preferred to use silica gel, other gels, such as gels of tungstic oxide, titanium oxide, stannic oxide, aluminium oxide, may be employed. If properly prepared the pores of these gels are so minute that it is impossible to measure their dimensions. However, one rule for determining whether the gel has the proper porous structure involves the amount of water vapour that the porous material will adsorb at a low partial pressure. Thus, an unimpregnated gel suitable for the present invention should have pores of such size that the

gel will adsorb water vapor to such an extent as to contain not less than about 10% of its own weight (when dry) of water when in equilibrium with water vapor at 30° C. and a partial pressure of 22 mm. of mercury. The best gels will adsorb water vapor to such an extent as to contain about 41% of their weight (when dry) under the conditions specified. Of course the gels impregnated with the dehydrating agents mentioned herein will take up more water than mentioned above.

55 The dehydrating agent with which the gel is impregnated may comprise any substance which will combine reversibly with water vapor. For example, the dehydrating agent may be strong sulphuric acid or metaphosphoric acid or a dehydrated metallic sulphate such as the sulphates of copper, aluminium, magnesium and the like.

70 The finely porous gel such as silica gel may be impregnated with the dehydrating agent in various ways. According to one method, the gel in its final state of manufacture, in granular form, while warm (say at a temperature above 300° F.), may be added to, or mixed with, a hot solution of the impregnating agent (say at a temperature above 150° F.). The mixture is allowed to stand for a time, say fifteen minutes or longer, and then the excess solution is drained or filtered off. Then the gel thus treated is dried, say, at a temperature of 400° F. for about three hours. If a lower temperature is employed, of course the drying will take a proportionately longer time. The object of this step is to partly dehydrate the impregnating compound and remove excess moisture from the gel. This step is one more of convenience and this and the following step may be incorporated into one step, that of activating at a temperature of 600° to 700° F. for three hours. The next step consists in activating the material for about three hours at a temperature of in the neighbourhood of 600° to 700° F. The object of this step is to put the impregnating compound in its most dehydrated condition and at the same time lower the

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residual moisture content of the gel itself to approximately 3% to 4% where the gel is most effective as an adsorbent. The material is now ready for use.

5 In the process just outlined, the silica gel and solution are taken hot because it is found that if they are brought together under these conditions, decrepitation of the granules is reduced to a minimum.

10 If sulfuric acid is used as the impregnating substance, it is best to use this in concentrated form rather than in dilute solution.

15 Silica gel impregnated with about 5% sulfuric acid by weight (calculated as 100% acid) gives very good results.

20 For the gels impregnated with the other substances mentioned, it is found that if the impregnating substance is present in an amount from 5% to 10% calculated on the dry weight of the gel, very satisfactory results are secured, although the invention is not limited to these exact quantities. For impregnating the gel with these dehydrating agents the granular gel is added to a solution of the agent of suitable strength. For example when copper sulfate is employed, a solution is taken preferably of about 30%  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  for a gel the residual  $\text{CuSO}_4$  content of which is to be approximately 10%. Copper sulfate is an ideal substance for impregnating the gel which is to be used to take up water vapor.

35 Copper sulfate normally contains five molecules of water of crystallization and passes over to the anhydrous form at 310° F. The anhydrous or partially dehydrated copper sulfate is an excellent dehydrating agent, since it will take up water until it again contains five molecules thereof. The temperature required to decompose copper sulfate into copper oxide and sulfur trioxide is approximately 1200° F. This temperature is in excess of any temperature necessary to reactivate the gel or to dehydrate the copper sulfate. It is for this reason that it is a particularly good substance for the present invention.

45 According to another method of obtaining the impregnated gel, the impregnating substance may be added to the gel in a preliminary stage of its manufacture.

55 In making silica gel, for example, if sodium silicate and acid solutions of the proper concentrations and amounts are thoroughly mixed, a liquid is obtained which is termed a "sol". The viscosity of this sol gradually increases and after a time the whole mass sets to a homogeneous jelly-like body which is termed a "hydrogel". This hydrogel is then broken into pieces, washed and dried.

60 The hydrogel contains over 90% water, whereas the final product has its moisture content reduced to a much lower amount, say 3% to 12%. According to this other method of making the product employed in this invention, the washed hydrogel, referred to above, may be immersed in a solution of the substance with which it is desired to impregnate the gel. The hydrogel will take up some of the solution, being allowed to remain immersed in the solution for a half hour or longer until the desired amount of the impregnating solution has been taken up. Then the impregnated hydrogel is dried in the same manner as when preparing the usual unimpregnated gel. For this purpose air at a temperature of around 120° C. may be passed over and around the pieces of the hydrogel and after a time this temperature may be increased slowly to 300° to 400° C.

65 This gives the finely porous hard gel as the resulting product. Finally the impregnated gel thus obtained may be further heated for about three hours or so at approximately 600° to 700° F. in order to fully activate the dehydrating agent.

70 No rule can be given as to just what the concentration of the solution should be in which the hydrogel is immersed. As an illustration, however, it may be stated that in order to obtain a final hard gel impregnated with, say 5% copper sulphate, the hydrogel should be 75 immersed in a copper sulphate solution of about 4.5% figured as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  for one to two hours.

To impregnate with metaphosphoric acid ( $\text{HPO}_3$ ) the warm dried gel, or the 80 hydrogel is immersed in a solution of orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ) and treated as previously described. The subsequent heating step or steps changes the orthophosphoric acid into metaphosphoric acid.

85 Gels impregnated with a dehydrating agent according to the present invention are particularly adapted for drying gases. They will dry such gases containing only 90 very small amounts of moisture. For 95 this purpose the gas is passed over the impregnated gel and it will be found for a considerable period of time that the impregnated gel will absorb 100% of the moisture in the gas. It will be seen that 100 this process is particularly applicable to drying air, such as air used for the blast of blast furnaces.

105 The impregnated gel of the present invention also has particular utility in connection with adsorption refrigerating plants where a liquid refrigerant such as brine is employed, and the impregnated gel of the present invention is used as 110 the adsorbent. In this case the adsorp-

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tion is effected at very low partial pressures, so low, that aside from silica gel and like gels there are no adsorbents that adsorb with sufficient rapidity to produce any practical amount of refrigeration. The impregnated gel of the present invention will take up more water in one of these refrigerating plants than the plain or unimpregnated gels. 5

10 Of course, in order to be practical for industrial uses, the impregnated gel must be able to withstand repeated regenerations or activations. It is found that the impregnated gels of the present invention may be repeatedly activated or regenerated, by heating, after adsorbing the water vapor, without appreciable decrease in their adsorptive efficiencies. 15

Although the invention has been described in detail, it is to be understood that it is not limited to the specific figures and amounts given, but includes modifications and changes which come within the scope of the appended claims. 20

25 Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

30 1. An adsorbent for water vapor, comprising a solid porous gel whose pores are of a size such that the gel will adsorb water vapor to such an extent as to contain not less than 10% of its own weight 35 of water when in equilibrium with water vapor at 80° C. and a partial pressure of 22 mm. of mercury, impregnated with a dehydrating agent, the adsorption capacity stated being that of the gel before 40 impregnation.

2. An adsorbent for water vapor, according to Claim 1, wherein the gel is silica gel.

3. An adsorbent for water vapor, comprising a solid porous gel whose pores are 45

of a size such that the gel will adsorb water vapour to such an extent as to contain not less than 10% of its own weight of water when in equilibrium with water vapor at 80° C. and a partial pressure of 22 mm. of mercury, impregnated with a substance which will combine reversibly with water vapor, the adsorption capacity stated being that of the gel before 50 impregnation. 55

4. An adsorbent for water vapor, according to Claim 1 or Claim 2, wherein the dehydrating agent is a deliquescent metallic sulphate, e.g. copper sulphate.

5. In the manufacture of an adsorbent for water vapor as claimed in Claim 1, the method of impregnating the gel which comprises mixing the gel in granular condition and at an elevated temperature (e.g. 300° F.) with a solution (preferably warm, say, at 150° F.) from which the dehydrating agent may be deposited in the gel, allowing impregnation of the gel with the solution to take place, removing the excess solution from the gel (e.g. by filtering) and heating the impregnated gel to dehydrate and activate it. 60

6. A method of drying a gas or vapor which comprises bringing the gas or vapor into contact with an adsorbent as claimed in Claim 1 or Claim 2 or Claim 3 or Claim 4, and thereafter heating the adsorbent to drive off its adsorbed moisture content and reactivate it for further 65 use.

7. The improved adsorbent for water vapor substantially as hereinbefore described. 70

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